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(54) RAPID PEEL SAUSAGE CASING CONTAINING PARTIAL ESTERS OF GLYCEROL OLEATE

(71) We, TEE-PAK, INC., a Corporation of the State of Delaware, United States of America, of 2 North Riverside Plaza, Chicago, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Artificial sausage casings made of regenerated cellulose have achieved wide success as a replacement or a synthetic substitute for natural casings in the processing of sausages, e.g., frankfurters, bolognas, and salamis. These casings typically are made by the viscose process wherein a cellulosic furnish is treated with caustic soda to form alkali crumb, the crumb shredded, aged, xanthated, and dissolved in caustic soda to form viscose, the viscose extruded through an annular die, and then the extruded casing coagulated and regenerated. The artificial sausage casings are shirred, i.e., lengths of from 40-200 feet of casing are compacted into a few inches, e.g., 4-30 inches. The shirred casings are packaged and sold to the meat processor wherein the casings then are stuffed with a meat emulsion, the meat cooked, and the casing removed from the meat processed therein.

It has been proposed to lubricate and internally humidify artificial sausage casings on a shirring machine by spraying a stream of water and a separate stream of lubricant in air through the shirring mandrel to increase the flexibility of the casing and to prevent breakage. Lubricants typically used in the shirring operation for aiding and assisting passage of the casing over the shirring mandrel include aqueous emulsions or dispersions of vegetable, mineral, or paraffin oil.

A variety of coating compositions have been applied over the internal surface of the sausage casing for improving the peelability of the casing from sausages processed therein. Many attempted solutions have been suggested by the prior art and have mainly involved the application of various coatings to the inner surface of synthetic cellulose casings to permit them to be peeled more readily from sausages. For example, fatty isocyanates, fatty ketenes, stearato chromic chloride, water-soluable silicones and polymerized silicones have been suggested as being release agents for cellulose sausage casings.

More recently, it has been proposed to coat the internal surface of a cellulose sausage casing with a homogeneous admixture of a water-soluble cellulose ether and an oil lubricant selected from the group consisting of animal, vegetable, mineral, and silicone oil or an alkylene oxide adduct of a partial fatty acid ester. The coating was applied to the casing surface in a proportion such that the lubricant was present in a proportion of at least 0.1 times the weight of the water-soluble cellulose ether and yet insufficient for providing more than 0.5 mg. per square inch of casing surface.

This invention provides a process for preparing an artificial sausage casing of regenerated cellulose having excellent peelability shirrability and anti-pleat lock characteristics which comprises applying a substantially homogeneous aqueous coating composition comprising a water-soluble cellulose ether, a mixed mono and diglyceride of oleic acid which may contain up to but not more than 10% by weight of triglyceride and having a capillary melting point not higher than 130°F. and water to the internal surface of said casing prior to shirring, said composition being applied in a proportion for providing from 0.01-0.1 mg cellulose ether and 0.01-0.1 mg of said mixed mono and diglyceride per square

inch of casing surface.

This invention also provides an artificial sausage casing of regenerated cellulose having its internal surface coated with a substantially homogeneous admixture of a water-soluble cellulose ether in the proportion of 0.01-0.1 mg per square inch and a mixture of mono and diglycerides of oleic acid having a capillary melting point not higher than 130°F. in the proportion of from 0.01-0.1 mg per square inch of casing surface.

Some of the disadvantages of early prior art coating compositions alleged to be useful for improving peelability of casings are that the coating compositions are not operable over a wide range of meat processing conditions experienced in the manufacture of frankfurters and have an undesirable frequency of breakage during shirring or during the stuffing operation. The more recent coating compositions which are alleged to be useful for improving peelability of casings, although having excellent peelability characteristics over a wide range of processing conditions sometimes have a tendency to jam on the shirring machine particularly when the coating composition is applied to small diameter casings (16 mm.). These casings also have some pleat lock characteristics which are undesirable. By undesirable pleat lock it is meant that the casing does not deshirr properly during the stuffing operation resulting in a high frequency of field breakage. Breakage due to pleat lock is presumably due to the undesirable adhesion of the nested pleats on the inside of the casing.

Advantages of the process for preparing sausage casings of this invention and the resulting casing include:

the ability to produce artificial sausage casings of regenerated cellulose having outstanding peelability over a wide range of processing conditions experienced in the meat industry;

the ability to shirr artificial sausage casings on high speed shirring machines without jamming or substantial frequency of breakage or damage;

the ability to produce shirred artificial sausage casings which can be readily deshirred under high speed stuffing operations without substantial tearing or pinholing of the casing;

the ability to produce shirred artificial sausage casings having excellent pleat lock characteristics so that the casing has sufficient handle to withstand normal handling required for providing end closures in the casing and placement in high speed stuffing machines without substantial breakage and yet undergo deshirring without pinholing or breaking; and

the ability to produce a humidified casing which does not "grow" substantially from its compacted state immediately after doffing.

In the manufacture of regenerated cellulose sausage casings viscose is extruded through an annular die into a coagulating and regenerating bath to produce a tube of regenerated cellulose. The tube is subsequently washed, plasticized with glycerin, and dried while inflated under a substantial air pressure for size control. After drying, the casing is wound on reels and subsequently shirred on high speed shirring machines, such as those described in U.S. Patents 2,010,626, 2,583,654, 2,722,714, 2,722,715 and 2,723,201.

To improve the peelability of sausage casings and to reduce the amount of breakage due to jamming on a shirring machine and reduce undesirable adhesion of the pleats during deshirring, it has been found that such improvements can be obtained when a casing of regenerated cellulose contains a coating over the internal surface thereof comprising a substantially homogeneous admixture of a water-soluble cellulose ether in the proportion of 0.01 - 0.1 mg per square inch and a mixture of mono and diglycerides of oleic acid having a capillary melting point not higher than 130°F in the proportion of from 0.01 - 0.1 mg per square inch of casing surface. In a preferred embodiment the coating includes a partial fatty acid ester of sorbitan or mannitan, preferably sorbitan.

It is believed that the water-soluble cellulose ether is the primary component for providing enhanced peelability of the casing whereas the mixture of mono and diglycerides of oleic acid aids in the lubrication of the casing during shirring and in providing anti-pleat lock characteristics to the shirred casing. It is the combination of the two components which gives the synergistic results noted in the reduced breakage of the casing during shirring and stuffing.

Water-soluble cellulosic ethers suited for practicing the invention include carboxymethyl cellulose, hydroxypropyl cellulose, methyl cellulose, ethylhydroxy ethyl cellulose, hyroxyethyl cellulose, carboxymethyl hydroxyethyl cellulose, and hydroxypropyl methyl cellulose. Quite often, the cellulose ethers are sold as the alkali metal salt and particularly the sodium salt. For purposes of this invention, reference to a water-soluble cellulose ether is intended to encompass the alkali metal salts. In a preferred embodiment of the invention, the water-soluble cellulose ether is a low molecular weight carboxymethyl cellulose having from about 5 - 15 carboxymethyl groups per 10 anhydroglucose

units.

The second essential component of the coating necessary for producing desired results in shirring and peelability of the casing is a mixture of mono and diglycerides of oleic acid (mono and diester). The mixed mono and diglycerides should have a capillary melting point of not higher than 130°F. and preferably have a capillary melting point of not substantially higher than 100°F. It has been found that when the capillary melting point of the oleic acid ester is higher than 130°F., there often is a coating of the shirring mandrel with the oleic acid ester which leads to increased jamming on the shirring machine and the frequency of breakage of the casing increases by about 25% over the breakage level experienced when the oleic acid ester of glycerin has a capillary melting point of about 100°F. or below. It has also been noted when the capillary melting point is above about 100°F. the shirred casing has reduced coherency to that made with a lower melting mixture of mono and diglycerides.

The mixture of mono and diglycerides of oleic acid contemplated for practicing this invention is to be contrasted with vegetable oils, even those having a melting point below about 100°F., as the vegetable oils are mixtures containing substantial proportions of triglycerides. There may be some partial fatty acid esters of glycerin in the vegetable oil including mixed mono and diglycerides of oleic acid but the amount of mixed mono and diester in these vegetable oils is much lower than is required for obtaining reduced breakage of the casing during shirring and during the stuffing operation. Generally, the vegetable oils do not have the effective lubricity that the mixed mono and diglycerides of oleic acid possess for permitting shirring with aqueous systems and more particularly they do not have the anti-pleat lock characteristics. As a result, casings having the coating comprising a cellulose ether and a vegetable oil do not produce the same results in shirring and stuffing in terms of reduced damage as a casing coated with a celullose ether and the mixed mono and diglycerides. The peelability characteristics of the casing, however, are substantially the same for both types of casing.

The mono and 'diesters of glycerin are partial esters comprising not more than 10% triglycerides. The proportion of monoester to diester may vary for producing a resultant mixture of mono and diglyceride having the desired capillary melting point range. Experimental evidence shows that a preferred ester combination is one containing from about 40 - 50% by weight, monoester, from about 40-50% diester, and the balance triglyceride and free fatty acid. It is believed the free hydroxyl group(s) on the mono and diester interact(s) with th cellulose casing to soften the surface of the casing to permit wet-out of the casing surface by the partial ester thereby enhancing the effectiveness of the ester as a lubricant for permitting high speed shirring without breakage and to reduce breakage during deshirring.

The coating composition which is applied to the interior of the casing surface preferably contains from about 0.5 - 2.5% by weight of a cellulose ether. This level of cellulose ether in the coating composition when applied at appropriate levels on the casing for effecting simultaneous humidification yields about 0.01 - 0.1 mg. cellulose ether per square inch of casing surface. In a preferred embodiment, the coating composition is applied to produce from about 0.03 - 0.06 mg. cellulose ether per square inch of casing surface. Application of the cellulose ether at levels below 0.01 mg. per square inch or above 0.1 mg. per square inch of casing is outside the scope of the present invention. Thus, levels of cellulose ether below 0.01 mg. per square inch on the interior of the casing surface often result in a casing having ordinary peeling characteristics. These casings cannot be considered a premium casing designed for high speed peeling operations where a "rapid peel" casing is required. When the level of cellulose ether exceeds 0.1 mg. per square inch of casing surface, then the surface of the frankfurter often becomes slimy. Some of the cellulose ether is transmitted to the meat surface at any of the levels present in the coating on the casing surface but excess cellulose ether on the casing surface results in an undue amount of transfer of cellulose ether onto the meat. Additionally, the higher concentrations of cellulose ether, i.e., those above 0.1 mg. per square inch of casing surface, do not seem to enhance peelability over coatings containing the prescribed amount of cellulose ether.

The proportion of mixed mono and diglycerides of oleic acid in making the coating composition is from about 0.2 - 2% by weight. When a coating composition is applied to the casing at appropriate levels, the mixture of mono and diester is present in a proportion of from 0.01 - 0.1 mg. per square inch of casing surface. Levels of mono and diglycerides of oleic acid below 0.01 mg. per square inch of casing surface do not have desired shirrability or anti-pleat lock characteristics. Levels of mixed mono and diester above 0.1 mg. per square inch on the casing surface tend to cause the casing to be fragile and difficult to

handle f r placement of an end closure therein or placement in high speed stuffing machines. Levels of ester from 0.03 - 0.06 mg. per square inch are preferred.

In a preferred embodiment of the invention a partial fatty acid ester of sorbitan or mannitan is included with the combination of water-soluble cellulose ether and mixtures of mono and diglycerides of oleic acid. The partial fatty acid ester of sorbitan or mannitan is included in the composition primarily for its lubricative properties. By a partial fatty acid ester of sorbitan or mannitan is meant the palmitic, oleic or stearic acid esters. In a preferred embodiment of the invention, the partial fatty acid ester is a sorbitan ester, preferably sorbitan trioleate.

The sorbitan or mannitan fatty acid esters may be included in the coating composition in a proportion of from about 0.25 to about 2% by weight. As a rule of thumb, as the proportion of mixed mono and diester is reduced toward the lower amount in the coating composition, e.g., 0.2% by weight, then the proportion of partial fatty acid ester of sorbitan or mannitan is increased toward the upper amount. This, in effect, gives the same effective proportion of lubricant for the coating of the casing. Likewise, where the proportion of partial fatty acid ester of sorbitan or mannitan, e.g., sorbitan trioleate, is reduced toward the lower amount, e.g., 0.25%, the proportion of mixed mono and diester is increased toward the upper amount, e.g., 2%. Levels of from 0.01 - 0.1 and preferably 0.03 - 0.06 mg. per square inch of casing surface are employed.

Thus, the aqueous coating composition is a homogeneous admixture containing from about 0.5 - 2.5% water-soluble cellulose ether, 0.2 - 2% mixed mono and diglyceride, and optionally 0.25 - 2% of a partial fatty acid ester of sorbitan or mannitan, and the balance is essentially water, and the coating composition is applied at desired levels for effecting simultaneous humidification of the casing as well as effecting coating of the casing for enhancing shirring and peelability of the casing.

As mentioned previously, the coating composition used in the process of this invention, in addition to imparting rapid peel characteristics, enhanced shirrability, and outstanding anti-peak lock characteristics to the regenerated cellulose casing, effects simultaneous humidification of the casing. As is known, the moisture content of the regenerated cellulose casing must be confined to a narrow range in order to shirr the casing as well as stuff the casing in the field without an undue amount of breakage. Regenerated cellulose casing having a low moisture content has a tendency to be quite brittle which leads to a number of pinholes and cracks. When the moisture level is too high, the casing has little resistance to stretch and becomes quite difficult to shirr. In casing manufacture, the moisture content of the casing is raised from a level of from about 8 - 10% in the dry reel stock to about 16 - 22% by weight of the casing at the time of shirring. In most commercial operations, the moisture content is adjusted to 18% ± 1% moisture concentration.

In applying the coating composition to the regenerated cellulose casing, the level of addition of coating composition is regulated so that it simultaneously humidifies the casing bringing the moisture content to a level of about 18% ± 1% by weight and yet applies an appropriate amount of the active components, within the ranges specified, for enhancing peelability of the casing, lubrication during shirring, and providing for anti-pleat lock characteristics. Of course, if humidification is supplied from a second source, then the coating composition may contain higher proportions of active components. However, there is a tendency to lose the effect of a uniform dispersion in the obtaining of a uniform coating and humidification in the casing when a separate humidification source is employed.

The coating composition should be applied to the casing prior to shirring and a number of ways are suited. It is possible to coat the interior of the casing by a slug technique which comprises introducing a quantity of the liquid into the casing either prior or subsequent to the drying operation. Slug coating of the interior of small diameter sausage casings, however, is not generally favored in commercial processes because of the high speeds involved and the difficulty in applying a uniform level of coating composition over the internal surface of the casing. Spraying the coating on to the interior of the casing immediately prior to shirring using the apparatus described in U. S. Patent 3,451,827 is much more effective and is easier to use for the coating of the interior of sausage casings and is preferred.

The following examples are provided to illustrate preferred embodiments of the invention and are not intended to restrict the scope thereof. All percentages are expressed as weight percentages. The words "Span" and "Tween" referred to are Registered Trade Marks.

EXAMPLE 1

Substantially homogeneous coating compositions having the following compositions are prepared:

Sample A (comparative sample) — 1%

carboxymethyl cellulose having an average substitution of 7 carboxymethyl groups per 10 anhydroglucose units commercially available as CMC 7LF from Hercules, Inc., 1.5% castor oil, and the balance water.

Sample B — 1% carboxymethyl cellulose having an average degree of substitution of 7 and an upper viscosity limit for a 2% water solution of about 18 centipoises at 25°C. commercially available as CMC 7L1 from Hercules, Inc., 1% sorbitan trioleate commercially available as Span 85 from Atlas Chemical, and 0.5% of a mixture of mono and diglycerides of oleic acid having a capillary melting point of about 115 - 120°F. commercially available as Dur Em 104 from the Glidden-Durkee Division of SCM Corporation and the balance water.

Sample C — 0.75% carboxymethyl cellulose (CMC 7L1), 1% Span 85, 0.5% of a mixture of mono and diglycerides of oleic acid having a monoglyceride content of about 46%, a diglyceride content of about 46%, and the balance consisting essentially of triglycerides of oleic acid and fatty acids. This mixture is commercially available as GMO D-2-2245 from the Glidden-Durkee Division of SCM Corporation and the balance water.

Sample D — 1% CMC 7L1, 1% Durkee GMO, and the balance water.

Sample E (comparative sample) — 1% CMC 7LF, 49% propylene glycol, and 50% water.

Sample F (comparative sample) — 1% CMC 7L1, 1% ethoxylated (20) sorbitan mono-oleate commercially available as Tween 80 from Atlas Chemical, 49% propylene glycol, and the balance water. This formulation is commercially used as a rapid peel formulation.

Sample G (comparative sample) — 1% Tween 80, 1% CMC 7LF, and the balance water.

Sample H (comparative sample) — 1% CMC 7L1, 1% Span 85, and the balance water.

Sample I (comparative sample) — 1% Tween 80, 1.25% CMC 7LF, 2% castor oil, and the balance water.

Regenerated cellulose casings are coated with each of the coating compositions prior to shirring by means of the apparatus described in U. S. Patent 3,451,827. The proportion of composition added to each casing is adjusted to produce about 0.04 mg. CMC per square inch of casing surface. The casings are stuffed with a meat emulsion suitable for making frankfurters and cooked and smoked under identical conditions.

Sample compositions A and E have a breakage rate (which included breakage at the shirring machine or the presence of pinholes during stuffing) in a proportion of from about 4 - 10 breaks per 100 strands stuffed. Water systems employing a vegetable oil as a lubricating agent do not shirr well. Samples F, G, H, and I have a breakage level of from about 2 - 4 strands per 100 strands stuffed. Samples B, C, and D have a breakage level of from 0.2 - 0.4 breaks per 100 strands stuffed. (Quite obviously, 0.2 - 0.4 breaks are a calculated breakage rate based on stuffing of more than 100 strands.)

Only sample compositions B, C, and D are suited for the shirring of small diameter (16 mm.) casings without excessive breakage, e.g. 1 - 3 breaks per 100 strands. All of the other compositions are unsuited for shirring this small diameter casing on the shirring machines employed. Even when additional lubricant in the form of a mineral-air spray is applied through the shirring mandrel for facilitating lubrication of the mandrel surface, the yields of acceptable casing are lower than are obtained by using samples B, C, and D as the coating composition. In coating small diameter casing with samples B, C, and D is is found to be advantageous to use additional lubricant at a level of about 0.05 mg. per inch square of casing to facilitate shirring.

Samples F, G, H, and I have damage levels much higher than samples B, C, and D either due to shirring or pleat-lock at stuffing. There is a tendency for the casing to pinhole during deshirring on a Frank-A-Matic (Trade Mark) stuffing machine. Apparently, the compositions containing a 1% proportion of Tween as opposed to a vegetable oil are particularly susceptible to pinhole development at the shirring machine.

All of the casings exhibit excellent peeling characteristics from the sausages processed therein and the number of peeling misses for sausages peeled on the same day range from about 0.2 - 0.8 misses per strand. When the sausages are peeled the next day the misses per strand range from about 0.04 - 0.3 misses per strand. There seems to be little difference in the peeling characteristics of any of the sausage casings tested.

EXAMPLE 2

A regenerated cellulose sausage casing is prepared by spraying a coating composition containing 1% CMC 7L1, 1% Span 85, 1% Dur Em 104, and the balance water onto the interior of the casing surface with the apparatus described in Example 1. Simultaneous with the spraying of the coating composition is the introduction of a lubricating composition consisting of 1% acetylated monoglyceride and the balance mineral oil in an air spray at a

level of 0.1 mg. lubricant per square inch of casing. The casings experience a higher degree of breakage on the shirring of small diameter casing than sample B, C, and D of Example 1 but less breakage than with other coating compositi ns A, E, F, G, H and I described in Example 1. The breakage level of larger code, e.g. 25 - 26 mm casing, is from about 0.2 - 0.4%. The strands are more fragile than the shirred strands made with compositions C and D in Example 1.

COMPARATIVE DEMONSTRATION A

For comparative purposes regenerated cellulose casing is prepared by coating the interior of the surface in the manner described in Example 1 with a coating composition comprising 2% CMC 7LF, 2% GMO D-2-2245, 2% Span 85 and the balance water at a level for providing 0.2 mg. CMC per square inch of casing surface. The resulting casings shirr extremely well and experience a low frequency of breakage. These particular casings are somewhat oily to the touch and fragile and operators have difficulty in placing an end closure in the casing.

Also, it is noted that the meat has a slimy appearance after peeling.

COMPARATIVE DEMONSTRATION B

A regenerated cellulose casing is coated on the internal surface in accordance with the procedure in Example 1 with a coating composition comprising 1% CMC 7LF, 3% GMO D-2-2245, 2% Span 85, and the balance water at a level for providing 0.1 mg CMC per square inch of casing surface. the casings shirr well but are oily to the touch and are more fragile than casings coated with samples B, C, and D in Example 1. It is difficult to place end closures in the casing and to place the casings in the hopper of a high speed stuffing machine without breakage.

EXAMPLE 3

When the procedure of Comparative Demonstration B is followed with the exception that the composition is applied at a level for producing 0.03 mg. CMC per square inch of casing surface the adverse defects in the casing noted above are mitigated. The casing shirrs well without substantial breakage.

WHAT WE CLAIM IS:

1. A process for preparing an artificial sausage casing of regenerated cellulose having excellent peelability, shirrability, and anti-pleat lock characteristics which comprises applying a substantially homogeneous aqueous coating composition comprising a water-soluble cellulose ether, a mixed mono and diglyceride of oleic acid which may contain up to but not more than 10% by weight of triglyceride and having a capillary melting point not higher than 130°F. and water to the internal surface of said casing prior to shirring, said composition being applied in a proportion for providing from 0.01 - 0.1 mg. cellulose ether and 0.01 - 0.1 mg. of said mixed mono and diglyceride per square inch of casing surface.

2. The process of Claim 1 wherein said coating composition includes a partial fatty acid ester being a palmitic, oleic or stearic acid ester of sorbitan or mannitan.

3. The process of Claim 2 wherein said partial fatty acid ester of sorbitan is sorbitan trioleate.

4. The process of Claim 3 wherein said sorbitan trioleate is applied in a proportion of from 0.01 - 0.1 mg per square inch of casing surface.

5. The process of Claim 4 wherein said cellulose ether is carboxymethyl cellulose.

6. The process of Claim 5 wherein said mixed mono and diglyceride comprises from 40 - 50% by weight monoester, 40 - 50% diester, and not more than 10% triester.

7. The process of Claim 6 wherein said water-soluble cellulose ether is applied in a proportion of from 0.03 - 0.06 mg. per square inch of casing surface, said mixture of mono and diglycerides is applied in a proportion of from 0.03 - 0.06 mg. per square inch of casing surface and said sorbitan trioleate is applied in a proportion of from 0.03 - 0.06 mg. per square inch of casing surface.

8. An artificial sausage casing of regenerated cellulose having its internal surface coated with a substantially homogeneous admixture of a water-soluble cellulose ether in the proportion of 0.01 - 0.1 mg. per square inch and a mixture of mono and diglycerides of oleic acid having a capillary melting point not higher than 130°F. in the proportion of from 0.01 - 0.1 mg. per square inch of casing surface.

9. The artificial sausage casing of Claim 8 wherein said interior coating on said casing includes a partial fatty acid ester being a palmitic, oleic or stearic acid ester of sorbitan or mannitan.

10. The artificial sausage casing of Claim 9 wherein said partial fatty acid ester of sorbitan is sorbitan trioleate.

11. The artificial sausage casing of Claim 10 wherein said cellulose ether is carboxymethyl cellulose.

12. The artificial sausage casing of Claim 11 wherein said mixture of mono and diglyceride comprises from 40 - 50% by weight monoester, 40 - 50% diester, and not more than 10% triester.

13. The artificial sausage casing of Claim 12 wherein said carboxymethyl cellulose comprises a proportion of from 0.03 - 0.06 mg. per square inch of casing sur-

face, said mixture of mono and diglyceride comprises a proportion of from 0.03 - 0.06 mg. per square inch of casing surface and said sorbitan trioleate comprises a proportion of from 0.03 - 0.06 mg per square inch of casing surface.

14. The process of Claim 1 substantially as described in Example 1 using coating composition B, C, or D thereof, Example 2 or Example 3.

15. The artificial sausage casing of Claim 8 substantially as described in Example 1 with a coating according to composition B, C or D thereof, Exampl 2 or Example 3.

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